Appraisal of polycyclic aromatic hydrocarbons (PAHs) in environmental matrices by analytical pyrolysis (Py-GC/MS)

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Abstract

Large number of studies has demonstrated the usefulness of flash pyrolysis in association with GC-MS in releasing diagnostic volatile compounds informing about the complex composition of natural organic matter (NOM). This knowledge is of interest as regards monitoring agricultural and environmental processes including pollution. In this context the term NOM comprises a wide array of biomacromolecules (lignins, polysaccharides, proteins, lipid polymers, etc.), as well as complex thre-dimensional macromolecules, either labile or recalcitrant, and which are referred to with generic terms such as Dissolved Organic Matter, Humic Substances, Black Carbon, etc. In this communication an updated overview on recent advances achieved by Analytical Pyrolysis in the structural characterization of recalcitrant/fossil/ NOM is presented, with particular focus in the detection of polycyclic aromatic compounds (PAHs) within complex organic matrices.

Keywords: Black carbon, Burning, Fire, Humic substances, Lignite, Pyrogenic organic matter, Soil organic matter

Introduction

Pyrolysis is the breaking apart of large molecules into smaller ones using thermal energy in the absence of oxygen. The combination of pyrolysis with separation and detection means is known as analytical pyrolysis. This technique is a powerful tool widely used for the direct characterization of organic mixtures with diverse origin which, owing to their complexity, are difficult to analyse by both conventional destructive or non-destructive methods. Pyrolysis is routinely used as a forensic tool to fingerprint or trace specific analytes within complex substances such as tyre rubber, textiles, paint, glue, paper coatings, petrochemical sources, or plant-derived materials including wood, coal and fossil remains, archaeological and cultural heritage artefacts, bacteria, and the whole range of synthetic polymers [1–5].

Pyrolysis of NOM generates a wide range of products with diverse structure that can be related to their biochemical origin. In particular, specific pyrolytic compounds from vascular plant debris are often monitored as tracers of the fate of the source material [6]. In the case of soil or sedimentary organic matter, analytical pyrolysis has enlightened crucial structural aspects in a wide range of substances from kerogens or peats to humic-like substances from composted organic matter [7–10], including soil organic matter [11–14], sedimentary organic matter [15–17], pyrogenic C-forms i.e., black carbon (BC) and other highly refractory forms of organic matter accumulated and transformed in soils and sediments, or newly-formed during forest fires [18–28].

This is the case with BC, which is understood as a continuum from partly charred plant material, through char and charcoal to graphite and shoot particles condensed from the

gas phase [29–31]. As biomass is charred, aryl and *O*-aryl structures (aromaticity) increase in concentration with a concomitant loss in carbohydrate and lignin structures [32]. Micromorphological and chemical features of this refractory material are described elsewhere [33–36]. Black carbon behaves as a highly aromatic material and, in the case of BC from vegetation fires [37], is considered to consist of randomly oriented stacks of few graphitic layers. In other cases BC is not necessarily graphitic, and this black material, even when completely amorphous, may contain both a substantial alkyl domain and oxygen content (endocyclic or lactone-like) structures [34, 36, 38]. Black carbon takes part in a variety of relevant environmental processes. Thus, it affects Earth climate though its light-absorbing effect, but it is also thought that BC may be part of the missing carbon in the global carbon balance [39–40 and references therein] as well as a carrier-phase of pollutants playing a key role in the sorption of contaminants including PAHs [41]. Although the molecular composition and source-depending structural variability of BC remain largely unknown, it is admitted that PAHs are its most typical discrete components.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous components of natural organic matter subjected to fire's impact or geothermal conditions. There are three major environmental sources of PAHs: combustion of organic matter (pyrogenic), petroleum (petrogenic) and natural sources including volcanism [42 and references therein]. While local areas can be impacted by petrogenic PAHs, combustion of organic matter is the largest source of PAHs to the environment with biogenic sources of PAHs limited to only a few compounds (i.e retene and perylene). In general it is considered that pyrolytic PAHs include all parent compounds other than retene and perylene, having MW> 178. Alkylated homologue PAHs usually derive from fossil sources [43–45]. In

any case, and as regards PAHs found in environmental matrices like soils, sediments or BC we could consider their origin either as native constituents or incorporated by sorption of allochthonous pyrogenic or anthropogenic products.

The environmental occurrence of PAHs is frequently underestimated by both wet chemical degradation or spectroscopic approaches, which often lead to patterns which are often meaningless from the structural viewpoint in which heavily polycondensed aromatic material often represent an 'invisible' domain, either by its frequent spectroscopic underestimation or the nonstoichiometric yields after chemical degradation [46]. In fact, frequent routine methodological approaches to study PAHs from geological samples are based on analyses of solvent extracts and further chromatographic separation [47–49]. However, detection of PAHs by direct pyrolysis of geological materials is feasible and has been reported [50–53], evidencing a series of advantages for the rapid examination of PAHs in whole sediments.

The main aim of this review study is to examine antecedents and the reliability of analytical pyrolysis techniques in evidencing the occurrence of PAH compounds in complex organic matrices. In addition, the potential of Py-GC/MS as analytical technique to detect PAHs in environmental samples was tested in a set of standard samples that has been thoroughly characterized by previous studies using non-destructive (e.g., ^{13}C NMR spectroscopy) techniques. These included charred biomass, soils, sediments, refractory organic matter (BC), soot, coal and lignite. PAH-lacking samples were used as negative controls.

Capability of pyrolysis tools and conditions for PAH analysis

Analytical pyrolysis has been used as a tool for the analysis of PAHs included in environmental matrices (i.e soil and sediments), as pollutants, constituents (i.e. coals and black carbon) or pyrogenic (i.e. chars and charred materials from forest fires). Medina-Vera [50] used a platinum coil pyrolyser to screen PAHs in pure standard mixtures and sediment samples. Adjusting the analytical conditions the author was able to thermally desorb (350 °C) the PAHs from sediment samples without any pre-treatment. The method was proved to be appropriate for the detection of compounds ranging from naphthalene to pyrene, which demonstrated that analytical pyrolysis is a suitable and convenient technique for PAHs screening in sediment samples [50]. A modification of this technique was developed by Faure and coworkers as a rapid contamination screening tool. The so called thermodesorption GC/MS (TdGC/MS) was found efficient for the rapid assessment of sediment contamination by free pollutants (especially by PAHs) with no interferences from possible cyclization and aromatization artifacts formed in the presence of clays in the media. It was also considered this technique as a valuable tool to provide crucial information to environmental agencies for long term management of rivers and sediments [51–52].

Terán et al. [16] used double shot analytical pyrolysis in a screening of organic contaminants in sediments from the South Iberian Penisnsula detecting series of linear alkylbenzenes (most probably from detergents), PAHs (petroleum or combustion products) and alkylnitriles with a probable origin in the industry and urban anthropogenic activities. They also established optimum pyrolysis temperature for pollution detection of these contaminants and demonstrated the usefulness of Py–GC/MS as a tool for rapid screening of organic contaminants in sediments. The same pyrolysis technique was also a very useful technique for the on-line determination of

PAHs in airborne particulate matter (soot/BC) trapped on cellulose filters without the need of using any sample pretreatment [53].

It has been found that Py-GC/MS pattern of coals is highly consistent with the chemical structure as inferred from NMR and elemental composition data. In fact the abundance of aromatics in the pyrolysates increased with coal rank in such a way that this could be used as coal rank parameter [54].

Curie point analytical pyrolysis and thermally assisted hydrolysis and methylation (THM) has been used to detect aged black carbon (BC) in soils. Kaal et al. [27, 28, 31, 37, 40] first studied ancient fire-affected organic matter thorough analytical pyrolysis and found a large proportion of PAHs, benzenes and benzonitriles in the pyrolysates of extractable soil organic matter derived from BC. They concluded that BC in soil conforms a partially oxidised, highly aromatic but weakly condensed network, containing significant amounts of N as previously suggested [55].

Recently González-Pérez et al. [56] used double shot pyrolysis to investigate organic matter evolution in lignite-rich acid mine soils. Apart from the normal markers produced by the recent OM, a wide range of PAHs were detected. These include natural PAHs like retene, considered a diagenetic product of dehydroabietic acid and a typical geochemical marker for lignite [57], and series of up to four benzene ring structures (pyrene) in the sediments. Traces of PAHs of up to five benzene rings were found in the Miocene lignite pyrolysates. Also major series of two-ring compounds mainly alkylnaphthalenes in addition to dibenzofurans and fluorene derivatives were found. The authors concluded that compounds present in the lignite substrate but lacking in the

vegetation pyrolysates i.e. alkylbenzene series, 1H-inden-1-one, 2,3-dihydro-3,3,4,5-tetramethyl-, as well as PAHs other than retene, were appropriate markers betraying the contribution from lignite to the soil/sediment organic matter.

Py-GC/MS of standard samples

Reference samples studied

The samples studied are indicated in Table 1 and consists of:

A) BC-rich materials; chars (chestnut wood and rice grass), obtained from dried biomass in an electric oven at 400 ºC for 5 h under inert atmosphere [58], a soot and a low bituminous coal consisting of *c.* 10% pyrogenic inertinite, the characteristics of which being described elsewhere [59].

B) Environmental matrices including polyaromatic hydrocarbons. A Cretaceous sediment (Barremian-Albian; 130–100 Million years, dated by micropalaeontological data) was studied, this corresponds to the Cerrajón Formation (South of Jaén, Spain) in the Baetic Cordillera. This stratigraphic unit is a shale composed mainly of silty marls with organic matter interbedded with several layers of sandstones [60–61]. In addition, three soils thought to contain PAHs were included in this group; two black isohumic soils (Vertisol and a Chernozem) [59] and a Rendolic soil from 'Sierra de Cazorla' (Southern Spain) affected or not by a forest fire [12] that is a frequent source of BC in Mediterranean environments.

C) Two black-coloured organic samples used as negative controls: a melanoidin produced from urea + glucose at 90 ºC for 30 days and a marine sediment (oxidation-

176 resistant organic matter fraction: ROM) from offshore Huelva (SW Spain) coast. As in
177 the above case, and despite its dark colour, after analytical characterization by ^{13}C NMR
178 no appreciable aromatic carbons were detected with the sample consisting of
179 predominantly non-hydrolysable material with strong aliphatic nature [59, 62].
180
181 *Conditions of the Py-GC/MS experiments*
182
183 Pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS) was performed using a
184 double-shot pyrolyzer (Frontier Laboratories, model 2020i) attached to a GC/MS
185 system Agilent 6890N. Unaltered ground samples (5–50 mg depending on C content)
186 were placed in small crucible capsules and introduced into the furnace, which was
187 preheated at 500 °C for 1 min. In certain experiments the final temperature was 800 ºC
188 and in this case it is detailed in the corresponding Figure caption. The evolved gases
189 were then directly injected into the gas chromatograph-mass spectrometer for analysis.
190 The gas chromatograph was equipped with a low-to-mid polarity-fused silica capillary
191 column (J&W Scientific) of 30 m × 250 μm × 0.25 μm film thickness (Ref. DB-1701).
192 The carrier gas was helium at a controlled flow of 1 mL min^{-1}. The detector consisted of
193 an Agilent 5973 mass selective detector, and mass spectra were acquired at 70 eV
194 ionizing energy. Compound assignment was achieved via single-ion monitoring for
195 various homologous series, via low-resolution mass spectrometry, and via comparison
196 with published and stored (NIST and Wiley libraries) data. Traces corresponding to
197 selected homologous series of chemical families were obtained by single ion monitoring
198 (SIM) of characteristic ions.
199

200 In order to validate the reliability of the Py-GC/MS approach to identify PAHs in a
201 large variety of reference materials, the results of a series of selected independent
202 experiments are described and discussed below.
203
204 *Release of PAHs from BC reference materials*
205
206 The pyrograms from BC-containing materials (lignocellulose-derived chars from
207 chestnut wood and rice grass), Vertisol and Chernozem soils, bituminous coal, urban
208 soot and the negative control reference material (melanoidin) are shown in Fig. 1. These
209 samples correspond to reference materials studied in a previous comprehensive
210 interlaboratory experiment aiming to quantify fire-derived carbon in soils and sediments
211 [59]. The results evidence that, with limitations inherent to the chromatographic
212 separations, analytical pyrolysis was successful in identifying a wide range of aromatic
213 hydrocarbons presumably released from the BC moiety including PAHs up to six
214 benzene rings (e.g. benzoperylene, C_{22}). No PAH, even at trace amount, was detected in
215 the negative control.
216
217 The pyrograms of oxidation-resistant organic matter from the coast of Huelva (SW
218 Spain) [62] reveals that this material has a strongly aliphatic nature, yielding *n*-alkanes
219 and *n*-fatty acids as major pyrolysis compounds whereas aromatics were practically
220 lacking, as corresponds to a marine origin. On the other side, the major pyrolysis
221 compounds from lignocellulose char consisted mainly of aromatic and heterocyclic
222 compounds like benzofurans that are well known pyrolysis products from incompletely
223 charred lignocellulosic materials/coal tars [63] in addition to a major levoglucosan peak
224 arising from the pyrolysis of carbohydrates in celluloses [64]. Solid-state carbon nuclear

magnetic resonance (^{13}C-CP/MAS-NMR) of the same samples complements [27] and, in this case, corroborates the pyrolysis results: this marine refractory material displays a main alkyl-C signal (45–0 ppm) whereas the spectrum from the lignocellulose char displayed a major peak in the aromatic C range (160–110 ppm).

Release of PAHs from Cretaceous sediments

The occurrence of PAHs in both recent and ancient sediments has been extensively reported. In fact, some individual compounds as well as PAH ratios are currently used as biogeochemical proxies for sediment characterization and palaeoclimate assessment [49, 65]. In this third experiment, a Cretaceous sediments is studied by direct Py-GC/MS.

The sediments released a wide set of PAHs including unsubstituted and alkylated homologues of phenanthrene, fluorene, anthracene, pyrene, perylene and coronene (Fig 3). The dominance of cata-condensed structures (i.e. benzo[*e*]pyrene, benzo[*ghi*]fluoranthene) over peri-condensed (i.e. benzo[*a*]pyrene, cyclopenta[*cd*]pyrene) is evident, suggesting a pyrolytic origin at high temperatures. Also, the observation that non-alkylated structures derived from phenantrene, dibenzothiophene and fluoranthene are predominant over their alkylated homologues (Fig 3) indicates a contribution of pyrogenic material to the organic matter in the sediment.

The PAHs distribution found from the Andalusian shale is similar to that previously reported for sites located far from pollution sources (i.e. high mountain lakes and deep

250 sea sediments), clearly pointing to an origin from natural pyrogenic material. The PAHs
251 pattern found was most probably the result of in situ combustions and/or deposition of
252 soot from forest fires during the frequent fire events in the Cretaceous [66].
253
254 *Release of PAHs from wildfire-affected soils*
255
256 Mediterranean forest is highly vulnerable to fire during the dry, hot summer months
257 where temperatures often exceed 40 ºC [67]. Forest wildfires contribute to the periodic
258 destruction of Mediterranean and Atlantic ecosystems in the Iberian Peninsula and are
259 considered the main disturbance in the Mediterranean basin [68–70].
260 It has been indicated that fires' impact in Mediterranean and Atlantic ecosystems may
261 be recognized by severe transformations of soil physical, chemical and biological
262 characteristics associated to qualitative and quantitative changes in the most functional
263 fraction of soil such as organic matter including biota [19, 71–72]. These changes may
264 negatively affect soil health and quality, favouring the occurrence of erosive processes
265 [73]. The assessment of the effects of forest fires on organic matter is one of the most
266 complex subjects in the systematic research of environmental impacts [74]. The
267 identification of biogeochemical markers for the occurrence of forest fire events, as well
268 as to monitor ecosystems recovery is important for planning environmental restoration
269 actions after wildfires [12]. Among the obvious candidates as tracers for the occurrence
270 of wildfires in soils are pyrogenic PAHs.
271
272 For this case study the identification of PAHs in soil was assessed in a comparative
273 manner between the fire-affected soil and the neighbour, non-affected one, with the
274 same pedological and physiographical characteristics. When comparing the ion traces

for diagnostic PAHs in whole soil pyrograms, structures from one to four or more aromatic rings were observed only in the fire-affected soil, being traceable down in the soil profile (0 to 20 cm depth) (Fig. 4). This fact, in addition to the higher relative abundance of three and four benzene rings PAHs observed in soil top layers of the fire-affected soil, indicates a strong modification of the soil organic matter, either directly by fire or by charred material inputs additions from the burned vegetation. The effect was clearer in the uppermost soil layers.

Conclusions

Usual methodologies to analyse PAHs are in general time-consuming, and have additional drawbacks such as the need of previous extraction steps with organic solvents. Pyrolysis in association with GC/MS has shown valuable potential in the structural characterization of many different biopolymers and geomacromolecules, evidencing PAHs series of up to seven benzene rings from environmental chemically complex matrices. These conspicuous series of PAHs were not detected in other recalcitrant natural substrates where ^{13}C NMR indicates an almost completely aliphatic nature. Although not a quantitative technique, analytical pyrolysis (Py-GC/MS) is proposed as a fast alternative approach to detect PAHs in environmental samples. Amongst the advantages are: minimum sample handling steps, thus precluding selective losses or sample contamination, speed of analysis and the need of small amounts of samples.

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TABLE CAPTIONS

Table 1. Materials used

FIGURE CAPTIONS

Fig. 1. Pyrograms at 800 ºC of selected reference materials: SIM traces for pyrogenic PAHs: m/z 178 (phenanthrene/anthracene); 202 (fluorene/pyrene); 228 (benzanthracene/chrysene); 252 (benzofluorene/benzopyrene); 276 (indenopyrene/benzoperylene) and m/z 85 for *n*-alkanes.

Fig. 2. Solid-state ^{13}C NMR spectra and Py-GC/MS total current ion pyrograms of BC sample isolated from a marine sediment (Huelva, Spain) and charred chestnut wood.

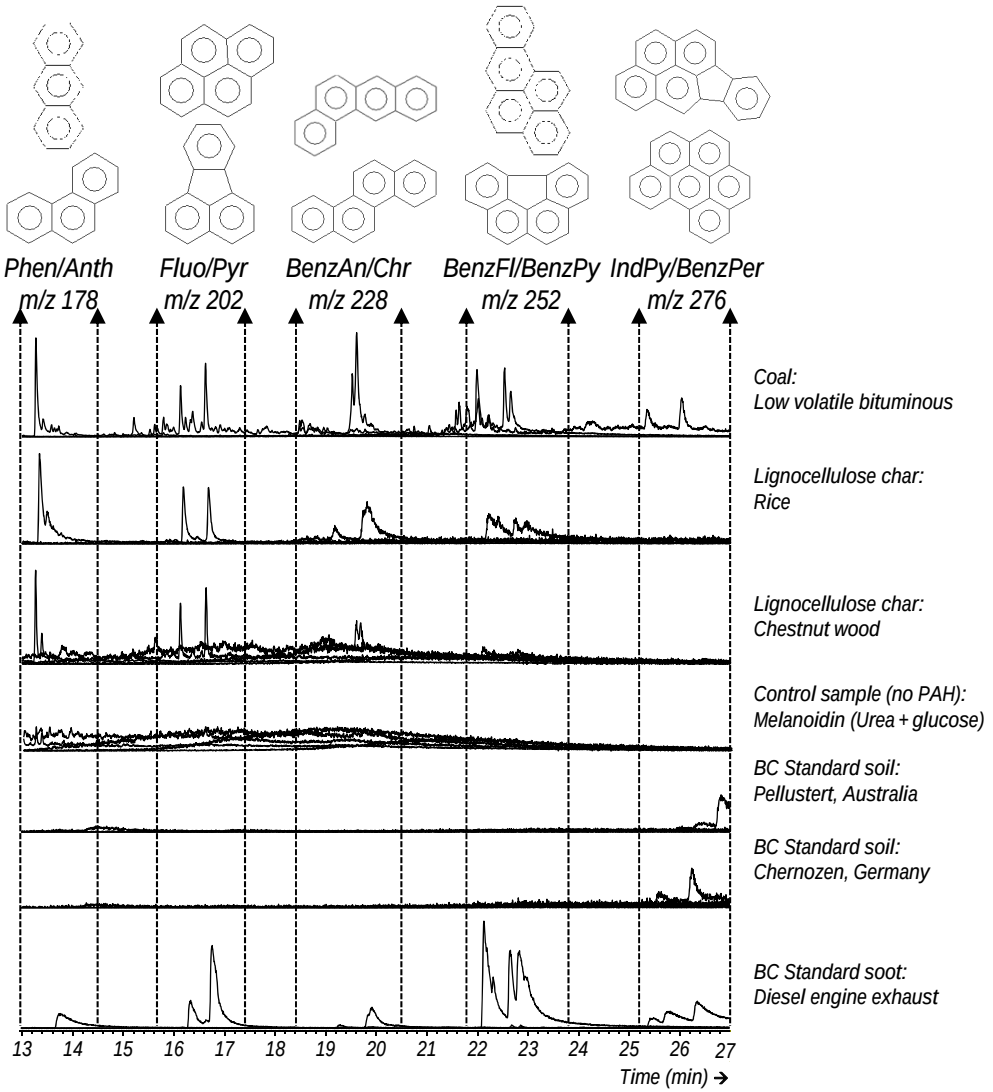
Fig.3. Series of PAHs identified by analytical pyrolysis (500 ºC) of Cretaceous sediment (shale) from the Cerrajón Formation (SE Iberian Peninsula).

Fig. 4. Analytical pyrolysis (500 ºC) of wildfire-affected and control, not affected soils from "Sierra de Cazorla" (S. Iberian Peninsula). Ion chromatogram traces (*m/z* 91 alkylbenzenes; *m/z* 178 three ring PAHs, *m/z* 228 four ring PAHs and *m/z* 252 five ring PAHs).

Table 1. Materials analysed

Material	Production/collection method	Rationale	Selected reference
	Group A: Natural samples and laboratory produced PAH-rich materials		
Soot: from *n*-hexane	Collected from the top of an *n*-hexane flame	Condensate produced from a fossil fuel	[52]
Char: Chestnut wood	*Castanea sativa* wood at 400 ºC for 5 h in N atmosphere	Char produced from hardwood biomass	[51]
Char: Rice grass	*Oryza sativa* straw at 400 ºC for 5 h in N atmosphere	Char produced from grass biomass	[51]
Coal: Low bituminous	From Buchanan County (Virginia, USA)	A mature coal (c. 10% pyrogenic inertinite)	[52]
	Group B: Environmental matrices		
Soil: Vertisol	Sandy clay soil from Urrbrae (Australia)	PAHs in soils	[51]
Soil: Chernozem	Light sandy soil from Harsum (Germany)	PAHs in soils	[51]
Soil: Rendollic soil	Soil on loess from Sierra de Cazorla (Jaén, Spain)	Pyrogenic PAHs from wildfire-affected soil (2005)	[12]
Sediment: Turbidite	Early Cretaceous formation from the Cerrajón (Jaén, Spain)	Turbidite with fossil pyrogenic PAHs	[56–57]
	Group C: Negative controls that contains no or low PAH content		
Melanoidin	Produced by heating urea and glucose at 90 ºC for 30 days	Negative control, contains no PAHs	[51]
ROM* sediment fraction	From offshore marine sediment (Southwest Spain)	Negative control, contains no PAHs	[58]

*) Organic matter refractory to wet oxidation at room temperature


Phen/Anth
m/z 178
Fluo/Pyr
m/z 202
BenzAn/Chr
m/z 228
BenzFl/BenzPy
m/z 252
IndPy/BenzPer
m/z 276
Coal:
Low volatile bituminous
Lignocellulose char:
Rice
Lignocellulose char:
Chestnut wood
Control sample (no PAH):
Melanoidin (Urea + glucose)
BC Standard soil:
Pellustert, Australia
BC Standard soil:
Chernozen, Germany
BC Standard soot:
Diesel engine exhaust
13
14
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16
17
18
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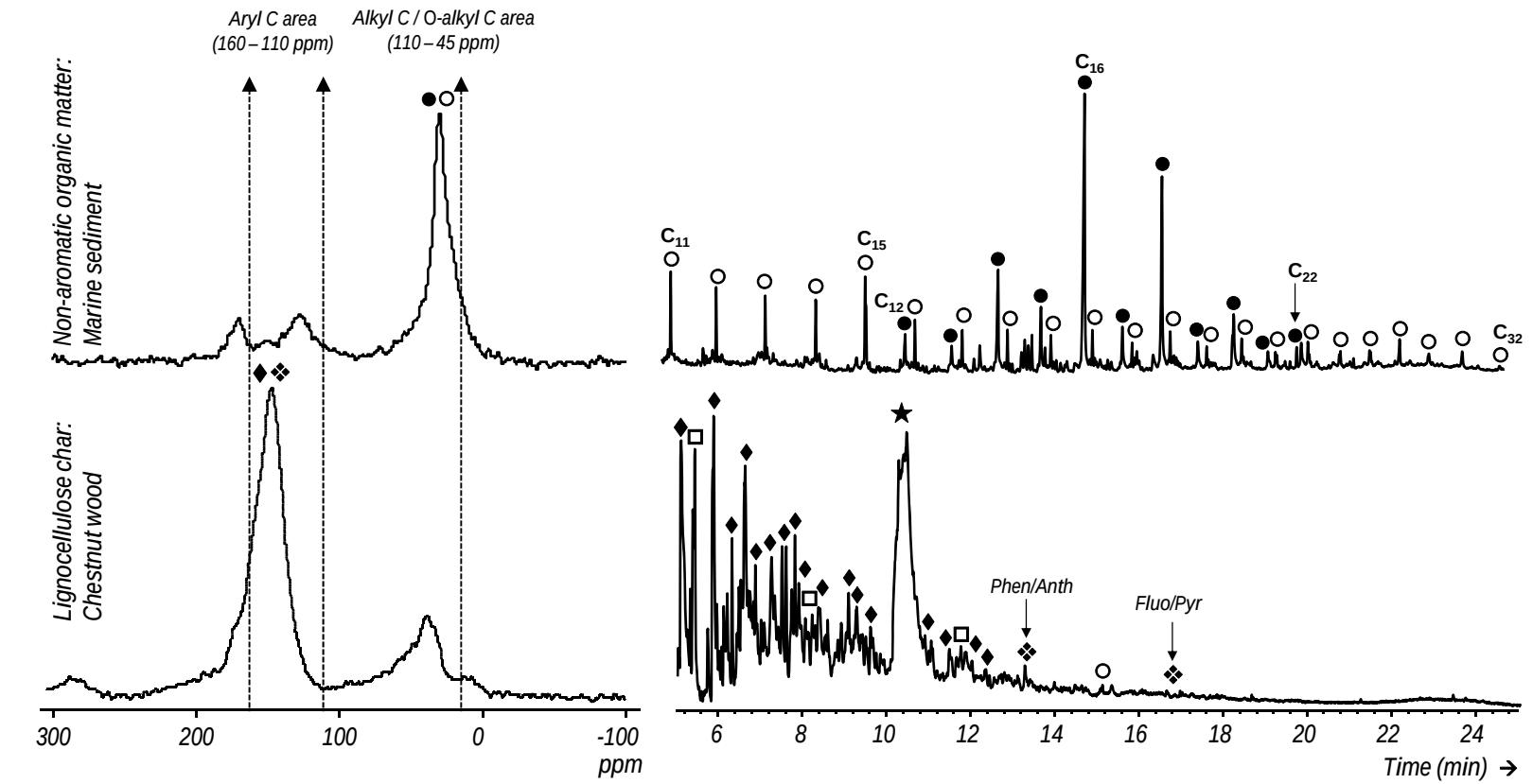
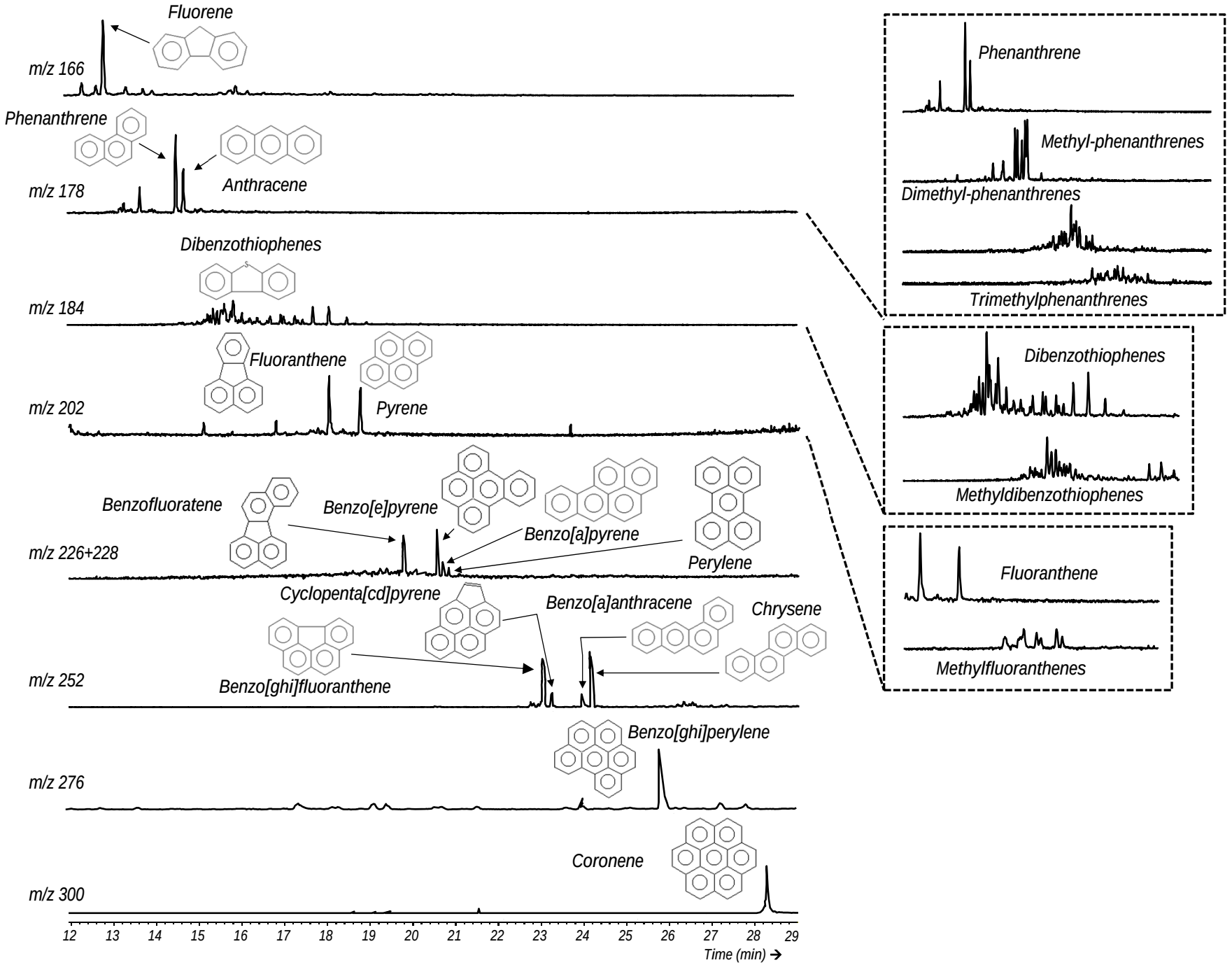
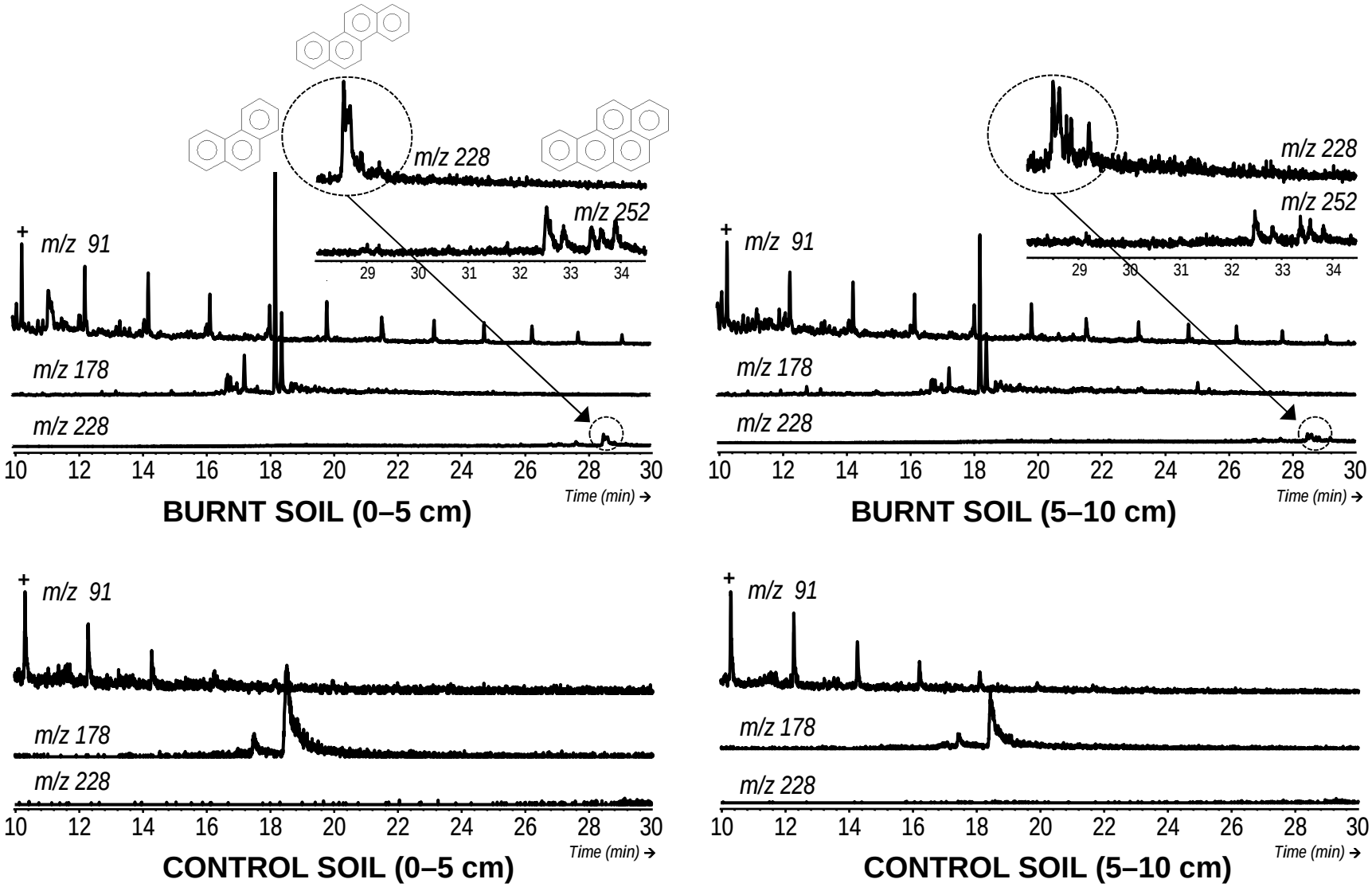
20
21
22
23
24
25
26
27
Time (min) →


Aryl C area
(160 – 110 ppm)
Alkyl C / O-alkyl C area
(110 – 45 ppm)
Non-aromatic organic matter:
Marine sediment
Lignocellulose char:
Chestnut wood
300
200
100
0
-100
ppm
C11
C12
C15
C16
C22
C32
Phen/Anth
Fluo/Pyr
6
8
10
12
14
16
18
20
22
24
Time (min)
○ n-alkanes
● n-fatty acids
□ Benzofuran derivatives
♦ Aromatic structures
❖ PAHs
★ Anhydrosugars


Fluorene
m/z 166
Phenanthrene
Anthracene
m/z 178
Dibenzothiophenes
m/z 184
Fluoranthene
Pyrene
m/z 202
Benzofluoratene
Benzo[e]pyrene
Benzo[a]pyrene
Perylene
m/z 226+228
Cyclopenta[cd]pyrene
Benzo[a]anthracene
Chrysene
Benzo[ghi]fluoranthene
m/z 252
Benzo[ghi]perylene
m/z 276
Coronene
m/z 300
12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
Time (min)
Phenanthrene
Methyl-phenanthrenes
Dimethyl-phenanthrenes
Trimethylphenanthrenes
Dibenzothiophenes
Methyldibenzothiophenes
Fluoranthene
Methylfluoranthenes



Traces are normalised with that of n-heptylbenzene (+)